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FINAL REPORT

AIR QUALITY SURVEY
FORT FRANCES, ONTARIO
SEPTEMBER, 1983

ARB-67-84-ARSP

April, 1984

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Ministry
of the
Environment

The Honourable
Andrew S. Brandt
Minister

Brock A. Smith
Deputy Minister

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PREPARED FOR THE
NORTHWESTERN REGION
MINISTRY OF THE ENVIRONMENT

By R.E. Chapman and G.B. DeBrou

Atmospheric Research and Special Programs Section
Air Resources Branch
Ministry of the Environment

APRIL, 1984

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TABLE OF CONTENTS

		Page
1.0	Summary	1
2.0	Introduction	3
3.0	MAMUs and Survey Strategy	4
	3.1 MAMU #2	4
	3.2 MAMU #3	4
	3.3 Survey Strategy	6
4.0	Results and Discussion	8
	4.1 Lagoon	9
	4.2 Boise-Cascade Kraft Mill (Can.)	12
	4.3 Boise-Cascade Insulite Plant (U.S.)	14
	4.4. Boise-Cascade Kraft Mill (U.S.)	15
	4.5 Chlorine/Chlorine Dioxide Measurements	15
5.0	Tables 1-10 and Figures 1-6	16-40
APPENDIX 1	Microbiology Report on Lagoon	41-46
APPENDIX 2	Gas Chromatography Results (Tables 11-12)	47-49
APPENDIX 3	Standards, Guidelines, Threshold Limit Values (Tables 13-14)	50-52

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1.0 Summary

During September, 1983, mobile air monitoring units from the Air Resources Branch carried out an air quality survey in Fort Frances, Ontario and International Falls, Minnesota. Boise Cascade Corporation and its Canadian subsidiary own two forest product manufacturing operations in that area which emit reduced sulfur and/or organic compounds into the atmosphere.

Monitoring near the secondary treatment system (lagoon) for liquid effluent from the Fort Frances kraft pulp mill was the highest priority during the survey. Air samples within a few metres of the lagoon were found to contain a reduced sulphur compound, dimethyl disulfide (DMDS), as the major identifiable component. Its concentration range was 40-70 ppb (parts per billion) for a 30-minute average. Dimethyl sulfide (DMS) was a minor component in the range of 10-15 ppb. Hydrogen sulfide (H_2S) levels were generally less than 10 ppb. Methyl mercaptan (MeSH) was probably not present. Residential areas immediately downwind of the lagoon usually had concentrations roughly 30% of the lagoon values. DMDS was the only reduced sulfur compound which exceeded its 1/2-hour standard (10 ppb) in the residential area, reaching a maximum value of 19 ppb. None of the organic compounds measured by gas chromatography exceeded or approached any of their 1/2-hour standards or guidelines. Monitoring by a TAGA 3000 mass spectrometer showed the presence of alcohols, aldehydes, ketones, organic acids, pinenes, and camphor, in addition to the reduced sulfur compounds, but none of the organic compounds were accurately quantified. Therefore, statements about the compliance of these compounds with Ontario standards or guidelines are inappropriate.

Total suspended particulate (TSP) levels were found to be above the 24-hour criterion of 120 ug/m^3 on the lagoon property on two warm, sunny days, but only 5 ug/m^3 on a cool, wet day. All off-property values were less than 120 ug/m^3, including four measurements in the nearby residential area and three at the control site 2 km away.

Several kinds of bacteria were found in a sample of dried foam at the edge of the lagoon. Very few bacteria of any type were isolated from filters exposed in high-volume samplers.

In the vicinity of the Boise-Cascade (Can.) kraft mill the major TRS (total reduced sulphur) component was MeSH. Thirty-minute average concentrations of this reduced sulphur compound ranged from 14-81 ppb, always in excess of the 1/2-hour standard of 10 ppb. DMS and DMDS were always less than 8 ppb. H_2S levels were always low, less than 10 ppb, except when the recovery boiler or lime kiln plumes impinged on the monitoring site. Areas within approximately 500 metres of the mill experienced TRS concentrations exceeding the TRS guideline (27 ppb). TRS results were generally consistent with data from the three fixed monitoring stations in Fort Frances. Concentrations of organic compounds (as measured by gas chromatography) were well below any of the 1/2-hour standards or guidelines.

A limited period of monitoring for chlorine and chlorine dioxide emissions from the Boise-Cascade (Can.) mill measured levels well below Ministry standards.

The small amount of data downwind of the Boise-Cascade (U.S.) kraft mill indicated that, in contrast to the Canadian mill, DMDS comprised a significant portion of the TRS compounds from the U.S. plant.

A white aerosol fog emitted by the Insulite plant in International Falls, Minnesota was investigated with the TAGA 3000. More than 50 organic compounds were tentatively identified but were not accurately quantified. Many of the compounds were naturally-occurring volatile substances found in wood.

2.0 Introduction

As requested by the Northwestern Region, the Monitoring and Instrumentation Development Unit of the Air Resources Branch conducted an air quality survey in Fort Frances, Ontario, and International Falls, Minnesota, during September 1983. The objective was to characterize the total reduced sulfur (TRS) and organic compounds being emitted from several sources: the Boise-Cascade (Can.) kraft pulp mill; the Boise-Cascade (Can.) secondary treatment system (lagoon) for liquid effluent from the kraft pulp mill; the Boise-Cascade (U.S.) kraft pulp mill; and the Insulite plant operated by Boise-Cascade in the U.S.

Mobile Air Monitoring Unit (MAMU) #2 was utilized to measure TRS, meteorological parameters, and perform gas chromatographic (GC) analyses for the organic compounds. MAMU #3, equipped with a TAGA 3000 mass spectrometer, was used to monitor individual components of the TRS parameter; namely, methyl mercaptan (MeSH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). A second function of the TAGA 3000 was to provide 'fingerprints' of the gaseous emissions from the secondary treatment system and the Insulite plant. This was the initial attempt to operate MAMU #2 and MAMU #3 together in a major TRS survey after the required speciation techniques had been developed for the TAGA system and a new TRS analyzer installed in MAMU #2. This circumstance, combined with the complex nature of the sources, yielded a body of data that could only be interpreted after months of laboratory experimentation and data analysis following the survey.

For several years there has been public concern that foam blowing from the surface of the Boise Cascade secondary treatment system (aeration lagoon) presented a public health hazard. A previous study in 1980 identified the predominant bacterial species in dried foam as Klebsiella pneumoniae. The present survey also included a single sample of dried foam which was analyzed for bacterial levels. Several high-volume samples were collected near the lagoon. Some samples were analyzed for total suspended particulate (TSP) matter and one was analyzed for bacterial levels.

3.0 MAMU's and Survey Strategy

Two mobile air monitoring units (MAMU) were utilized in the Fort Frances survey. Each unit is a self-contained mobile laboratory equipped with advanced analytical instrumentation dedicated to ambient air monitoring. The specific functions of each mobile unit are unique and vastly different. MAMU #2 measures 'classical' pollutants, such as NO_x, SO_2, TRS, O_3 and specific hydrocarbons, while the MAMU #3 obtains real-time measurements of a large number of individual organic and inorganic contaminants. The present survey took advantage of the special capabilities of both units.

3.1 MAMU #2

The instrumentation of the MAMU #2 essential to this study were the TRS analyzer and the gas chromatograph (GC). TRS measurements were made by a Monitor Labs Fluorescent SO_2 Analyzer (model 8850) in conjunction with a Monitor Labs H_2S Converter (model 8770). During the survey, the Monitor Labs equipment was spanned with an H_2S source (Hartmann and Braun) to generate a calibrant mixture of 0.27 ppm H_2S in zero air. The TRS analyzer was calibrated each morning prior to any monitoring.

The MAMU #2 was outfitted with a modified gas chromatograph (Hewlett-Packard, 5840) coupled to a organic preconcentrator of our own design. Ambient air is drawn at 30 ml/min through a 6 mm O.D. glass cartridge containing absorbent Florisil, Molecular Sieve 13X and Spherocarb. GC sampling periods were 30 minutes so that the data could be directly compared to Ministry standards and guidelines. Contaminants trapped by the absorbents are thermally desorbed, prefocused and cryo-trapped at the GC column head. The sample was analyzed with a 50-meter cross-linked SE 54 column and a standard, flame-ionization detector. Compounds detectable by the GC preconcentrator system include alkanes, alkenes, alkynes, aromatics and chlorinated hydrocarbons. Typical detection limits are in the 1-10 ug/m^3 range.

3.2 MAMU #3

The MAMU #3 contains a single analytical instrument, the Trace Atmospheric Gas Analyzer, model 3000 (TAGA 3000). This unit is the most advanced and sophisticated mobile air monitor presently operated by the Ministry of the Environment.

Basically, the TAGA 3000 system is a single quadrupole mass spectrometer coupled to an atmospheric pressure chemical ionization (APCI) ion source. Figure 1 shows a schematic of the fundamental features of the TAGA 3000 system. Ambient air is sampled at high flow rate (1.5 litres per second) directly into the APCI ion source. Contaminants carried by the air stream are selectively ionized so that they can be readily extracted from the gaseous matrix and mass analyzed by the quadrupole mass filter. The entire process of sampling and analysis for a particular contaminant occurs in less than a second.

Specific chemical classes can be selectively monitored through the controlled addition of the appropriate chemical ionization (CI) reagents. For this particular study, benzene was used to ionize dimethyl sulfide and dimethyl disulfide. Methyl mercaptan was observed via a novel technique known as ozonalysis, where an ozone source (UV lamp) is placed directly into the sampling line. Unfortunately, the technique is not specific to monitoring MeSH in the presence of DMS and DMDS. Therefore, accurate MeSH measurements are possible only when the relative concentration of DMS and DMDS is low. As will be shown in this study, low DMS and DMDS concentrations were encountered near the Boise Cascade kraft mill (Can.) and thus MeSH levels could be determined. In contrast, near the aeration lagoon, the DMDS levels were significant and MeSH could not be detected above the DMS and DMDS interference.

The actual data generated by the TAGA 3000 are collected in two fundamental modes: (a) the mass scan or MS mode, where the air sample is screened over a wide mass range (10 to 250 amu); and (b) the real-time selected ion (pollutant) or SIM mode. The MS mode generates data in the form of mass spectra which provide a 'fingerprint' of the air sample. In the SIM mode, specific target contaminants are continuously monitored in real-time. The SIM mode is particularly useful for identifying sources via plume tracking techniques.

The instrument and the data acquisition process is controlled by a dedicated computer system. The information is instantly displayed on a monitor, allowing the operator to assess the data on-site and formulate the appropriate survey strategy. All data can be stored permanently on floppy disks for subsequent analysis.

Instantaneous mass spectral information can be obtained for a large number of organic and inorganic gaseous contaminants. Essentially, the TAGA is sensitive to any volatile compound containing at least one of the following atoms: S, N, O or halide. Detection limits vary greatly with contaminant, CI reagent and matrix complexity. Typical detection limits for sulfur compounds are in the 'few' ppb range. The TAGA, when equipped with the standard APCI front-end, does not observe aliphatic hydrocarbons; nevertheless, these compounds are detectable by the GC (MAMU #2). As in the MAMU #2, the MAMU #3 is outfitted with meteorological instrumentation: wind speed, wind direction, and air temperature are measured at a height of 10 meters using a telescopic tower.

3.3 Survey Strategy

A sound survey strategy is of primary importance to any air monitoring study, especially when mobile units are available and monitoring activites can rapidly change. Naturally, the overall survey strategy was designed to meet the objectives of the study as presented by the Northwestern Region.

Daily monitoring strategy was based on the following: (1) status of specific tasks; (2) meteorology; (3) source locations; (4) accessible roadways; (5) analytical capabilities and limitations; (6) plant operations; (7) plume presence; and (8) human resources and study time scale.

When possible during the survey, the MAMU #2 and MAMU #3 sampled simultaneously in the same general locations. In this way the TRS measurements made by MAMU #2 and the individual components measurements made by the TAGA could be compared. Also, since the TAGA and GC are sensitive to different chemical classes, sampling by both MAMUs ensures a more complete screening of the air for a wide range of potential contaminants.

All days of significant monitoring periods were ended with brief periods of background monitoring, well removed from any of the sources, as a quick check of proper instrument operation.

Being the top priority, the secondary treatment system (lagoon) located at 8th Street and Cornwall Avenue, Fort Frances, was our primary focus. When winds were northerly, monitoring was conducted at the lagoon (see Figure 2) and residential areas to the south, until at least 4 days of data were accumulated. Measurements were made for sulfur compounds in addition to "fingerprinting" emissions at the lagoon inlet and near the aerators.

On two occasions, teflon tubing was connected to MAMU roof inlet ports to sample the air directly above the lagoon surface. The purpose was to enhance the signal-to-noise ratio of the measurements for compound identification.

A grab sample of dried foam was collected from the edge of the aeration lagoon and sent to the Ministry's Thunder Bay Regional Laboratory for bacteriological analysis. In addition, sterile high volume filters were exposed at the lagoon and at a control site 2 kilometers away. Filters were then analyzed for bacteria by the Thunder Bay Regional Laboratory. Regular glass-fibre filters were exposed adjacent to the sterile filter and at two sites in the residential area near the lagoon; these filters were analyzed for total suspended particulate (TSP). The results of the bacteriological analyses are briefly discussed in section 4.1.7, and the complete report is contained in Appendix 1.

The Boise-Cascade (Can.) kraft mill was the second priority source. Monitoring of the source was usually performed during periods of southerly winds, thereby avoiding emissions from the Boise-Cascade (U.S.) plant.

Sampling site locations were based on the real-time plume tracking results of preselected target compounds characteristic of the source in question. Methyl mercaptan was used as a tracer for the Boise-Canada (Can.) Kraft mill while dimethyl disulfide proved to be an excellent tracer for the secondary treatment system. Coincident with all sampling periods was the presence of 'sulfurous' odours.

In addition to measurements of sulfurous species, the Region requested measurements for chlorine (Cl_2) and chlorine dioxide (ClO_2) from the Canadian kraft pulp mill. Due to the high variability of the Cl_2/ClO_2 emissions it was felt that monitoring Cl_2/ClO_2 would be a 'hit and miss' situation. Thus, this task was given low priority. Ideally, several weeks of continuous monitoring may be required to obtain a representative measurement of the ambient levels of Cl_2/ClO_2.

The third priority task involved 'fingerprinting' air quality near the Insulite plant in International Falls, Minnesota. The strategy was to sample ambient air during an emission release when a low-level white aerosol fog fumigated the area directly downwind of the plant. At the onset of these fog periods the TAGA and GC commenced collecting air samples. The GC sampled ambient air for one-half hour while TAGA accumulated several mass scans over a period of a few minutes.

The Boise-Cascade (U.S) kraft pulp mill was the lowest priority source and therefore only brief periods of survey time were available for that task.

4.0 Results and Discussion

The results of the study are summarized in Tables 1-10 and grouped according to source. All results presented here are downwind measurements in the sense that every attempt was made to be in the plume impingement zone. Selection of sampling locations was based on the real-time tracking data acquired by the MAMU #3 and the detection of odours. The locations of all monitoring sites for the reported half-hour averages are shown in Figure 2.

The results for TRS and its components MeSH, DMS, DMDS and H_2S require some background information for complete understanding. Until the present survey was in progress there was no reason to doubt the manufacturer's specified conversion rates of greater than 95% for the H_2S-to-SO_2 converter (Monitor Labs Model 8770) in MAMU #2. The conversion efficiencies of the other reduced sulfur compounds were believed to be in the range of 40% to 90%. After several periods of monitoring adjacent to the TAGA 3000 (MAMU #3) it became clear that the Model 8770 H_2S converter was converting reduced sulfur compounds to SO_2 at rates significantly lower than expected. Laboratory testing has since shown the efficiences of TRS conversion to SO_2 to be as listed in the heading of Table 1 for the various compounds. Conversion of H_2S was found to be only 70% instead of 95%, MeSH conversion was 45% and DMS conversion was 12%. Also, the SO_x scrubber, which was used to eliminate the interference due to ambient SO_2 levels, was found to scrub much of the MeSH and DMS. DMDS has not been tested yet, due to the lack of a suitable calibration source, but an estimated conversion rate of 20% has been used here, based upon the conversion efficiences presented here for the other TRS components and a previous study (report AQM/IU/82-3) by the AQM section of the Air Resources Branch. Measurement of the actual DMDS conversion efficiences is now in progress and the results will be forwarded to the Northwestern Region when available.

The results in Table 1 were obtained in the following manner: MeSH, DMS and DMDS were measured by the TAGA 3000 system with the limitations discussed in section 3.2; after applying the conversion efficiences to those three component concentrations some estimate of the H_2S concentration was obtained by subtracting the reduced sum of the MeSH, DMS and DMDS components from the measured TRS concentration and correcting the remainder for the H_2S conversion efficiency; the H_2S concentration was added to the MeSH, DMS and DMDS concentrations to form the adjusted TRS concentration.

Some of the contaminants measured during this survey are expressed as parts per billion (ppb) by volume while others are more appropriately expressed in micrograms per cubic metre (ug/m^3). Conversion from ppb to ug/m^3 (and the reverse) can be accomplished by referring to Table 13 (Appendix 3), which also includes the appropriate provincial standards and guidelines for these contaminants. Threshold limit values (TLV's) -8-hour exposure limit in the workplace - are listed in Table 14 for those contaminants without a standard or guideline.

4.1 Lagoon

4.1.1 Total Reduced Sulfur Components

Air samples within a few meters of the lagoon (Table 1) were found to contain dimethyl disulfide (DMDS) as the major identifiable component. The concentration range was 40-70 ppb (154-270 ug/m^3) for a 30 minute average. Dimethyl sulfide (DMS) was a minor component in the range of 10-15 ppb and methyl mercaptan (MeSH) appeared to be not present. (In the presence of relatively high concentrations of DMDS, as at the lagoon, we are not able to unambiguously measure MeSH.) Residential areas immediately downwind of the lagoon usually had concentrations roughly 30% of the lagoon values. This difference was consistent with the difference in relative odour intensities at the lagoon and in the residential areas. The H_2S level was usually only a few ppb near the lagoon, but reached 15-20 ppb at the lagoon surface, as shown by the results for site 16.

As a result of the large DMDS contribution to the TRS levels, the 30-minute TRS guideline (27 ppb) and DMDS standard (10 ppb) were exceeded for all sampling periods on the lagoon property. The DMDS standard (10 ppb) was exceeded for three out of seven periods in the residential areas, reaching a maximum of 19 ppb.

Uncertainty of TRS guideline exceedence in the residential area is due to the derived H_2S component of the adjusted TRS levels.

4.1.2 Gas Chromatography Results - Lagoon

The GC results in Table 2 (1/2-hour average concentrations) are for those periods when both monitoring units were in the same location, and together with the corresponding TAGA instantaneous results in Tables 3a and 3b comprise the most complete data set at the lagoon site. The entire set of GC results is included in Appendix 2.

None of the contaminant concentrations in Table 2 or in Appendix 2 exceeded or approached any applicable 1/2-hour standards or guidelines.

4.1.3 TAGA 3000 Fingerprint of Lagoon Emissions

On September 11, 13 and 22, 1983, mass scans (MS) were taken of the lagoon emissions at locations downwind of the effluent inlet and the aerators.

Analyses of MS scans are provided in Tables 3a (positive mode) and 3b (negative mode). There was strong evidence for the presence of alcohols, aldehydes, ketones, organic acids, pinenes, camphor, as well as DMS and DMDS. The TAGA system is extremely sensitive to these classes of compounds and this is reflected in the estimated concentrations. It should be noted that these estimates are based on instantaneous responses and not on averages. Therefore, they cannot be directly related to Ontario guidelines or standards. The major detectable contaminants were dimethyl sulfide, methanol, formic acid/formaldehyde and acetic acid/acetaldehyde. Detailed quantitative work would be required to determine accurate levels of these compounds. However, based on the instantaneous values, it is very unlikely that provincial standards would be exceeded.

4.1.4 TAGA 6000 Fingerprint of Lagoon Sample

In early December 1983 a lagoon sample (liquid) taken during the survey near the inlet was analysed at Sciex Inc., developer of the TAGA system, using the advanced TAGA 6000 MS/MS system. The TAGA 6000 system is basically a TAGA 3000 with a second mass analyzer and library search capabilities, enabling positive identification of the mass peaks that comprise a 'fingerprint'.

The TAGA 6000 was operated under conditions similar to those for the TAGA 3000 at the time of the survey; that is, with the same ionization reagents and atmospheric pressure sampling. Analysis was performed on the vapors above the liquid lagoon sample and the following compounds were identified: methanol, acetone, propanol, acetic acid, dimethyl sulfide, dimethyl disulfide, hydroquinone, pinenes and camphor. With the exception of hydroquinone, these same compounds were tentatively identified in air samples taken by the TAGA 3000 at the lagoon site.

4.1.5 Plume Tracking: DMDS (Lagoon)

The real-time measuring capabilities of the TAGA unit are well suited to obtaining plume concentration plots of target compounds. The data is useful for locating sources and choosing monitoring sites for 1/2-hour average determinations. Shown in Figure 3 is an example of the plume tracking data for DMDS acquired on September 29, 1983, between 10:55 and 11:30 hrs. The MAMU #3 was driven in a grid pattern downwind of the Boise-Cascade lagoon to obtain instantaneous measurements of DMDS every 2 seconds. The stars in Figure 3 represent positions where the data was flagged by the TAGA operator using the system's computer. Isopleths have been drawn on Figure 3 to accentuate the plume patterns. The isopleths assume that DMDS emissions and meteorological conditions were constant throughout the period of data acquisition.

The data clearly supports two important conclusions: first, that the source of DMDS is the lagoon; and second that the area of impact is broad and extends, at least, south to 5th Street and west to McIrvine Road. Of course, the pattern in Figure 3 is valid only for the time period indicated; other patterns can be expected for different source strengths and meteorological conditions. It should also be noted that the Figure 3 measurements are instantaneous and, therefore, cannot be compared to a half-hour standard. However, even instantaneous levels at the concentrations reported would be significant to the odour receptor.

4.1.6 High Volume Sampling

Early in the survey, some samples were collected with standard high-volume samplers in the residential areas nearest the lagoon. The results (Table 4) revealed a maximum TSP (total suspended particulate) level of 41 ug/m^3.

Later in the survey two hi-volume filter stations (HV* on Figure 2) were established to compare the amount of TSP at the lagoon with the amount at a control site in the cemetery 2 km to the south. The largest TSP level was 419 ug/m^3 at the lagoon site on September 26 while the simultaneous TSP level at the cemetery was 112 ug/m^3. On September 27 the lagoon site showed 148 ug/m^3 while the cemetery had 57 ug/m^3. The lagoon TSP values exceeded the 24-hour criterion (120 ug/m^3) and one filter (for September 26) showed a large amount of airborne dried foam. The period of September 26 to September 28 was sunny and warm with light winds. Another pair of filters was exposed on October 2 but the TSP and dried foam levels were minimal because the period from October 1 to October 3 was cool and wet. All TSP values off lagoon property were less than 120 ug/m^3, including the four measurements in the nearby residential area and three at the control site.

4.1.7 Bacterial Results

On September 14, a grab sample of dried foam was collected in a wide-mouth jar and sent to the regional laboratory for bacterial analysis. Several bacterial groups were recovered from this sample. Klebsiella pneumoniae, the predominant organism isolated from similar samples in the same area in 1980, was not found in the 1983 sample.

At the lagoon and the cemetery, hi-volume samplers were also operated with sterile filter cartridges. These were operated on September 26, 27 and October 2 for the same periods used for the TSP measurements. The sterile filters were later physically examined and suitable ones analyzed for bacterial content. While extremely low levels of bacteria were recovered from the material on the hi-volume filters, the sampling method probably did not favor the survival of viable bacteria.

The complete microbiological report is contained in Appendix 1.

4.2 **Boise-Cascade Kraft Mill (Can.)**

4.2.1 Total Reduced Sulfur Components

Near the Boise-Cascade (Can.) kraft mill the major TRS component was MeSH. Thirty-minute average concentrations of this compound ranged from 20 to

80 ppb (40 to 160 ug/m^3). DMS and DMDS were always less than 8 ppb, as seen in Table 5. When the 45% conversion efficiency was applied to the MeSH numbers, then all of the measured TRS was accounted for during many of the sampling periods. This means that H_2S was rarely present in the monitored areas. One exception was site 41, when the recovery boiler plume was impinging. On that occasion, the H_2S concentration was estimated to be as high as 29 ppb and the MeSH level was only 7 ppb. For site 31, the H_2S level was also significant, and the lime kiln plume was considered the most probable source.

As noted in section 3.2 the MeSH results are accurate because the DMS and DMDS levels are low. For the same reason, the adjusted TRS values incur only small errors by determining the MeSH/DMS/DMDS fractions during successive 1/2-hour periods in the TAGA system's negative and positive modes. The adjusted TRS concentrations frequently exceeded the 1/2-hour guideline due mainly to the large MeSH component. Figures 4 and 5 show the concentrations of TRS and MeSH measured at various distances from the kraft mill. Areas within approximately 500 metres of the mill experienced TRS concentrations exceeding the TRS guideline (27 ppb). TRS results were generally consistent with data from the three fixed monitoring stations in Fort Frances which has been reported regularly in the Ministry's annual air quality reports.

4.2.2 Gas Chromatography Results - Kraft Mill (Can.)

The results in Table 6 represent the only periods when any of the organic compounds were above their detection limits near the kraft mill. There was a strong mercaptan odour during each period, as indicated by the Table 5 results, but the concentrations of organic compounds did not approach any of the 1/2-hour standards or guidelines.

4.2.3. TAGA Fingerprint of Boise-Cascade Kraft Pulp Mill (Can.)

A fingerprint mass scan was taken on September 23, 1983 at 11:03 hrs. The location was Portage Ave. and Nelson Street downwind of the mill; odours were present. Analyses of the mass spectra are summarized in Tables 7a (positive mode) and 7b (negative mode). Contaminants detected included methanol, dimethyl sulfoxide, dimethyl sulfide, toluene, dimethyl disulfide, chlorine and chlorine dioxide. Again, the concentrations are based on instantaneous signals and are very crude estimates, possibly in error by as much as an order of magnitude. This data was acquired to supplement the GC data of Table 6, Set #5.

4.2.4 Plume Tracking: MeSH (Boise-Cascade Kraft Pulp Mills)

When two sources with similar emissions are in close proximity, plume tracking is essential for selective monitoring of the source of interest. In the Fort Frances/International Falls area, the two kraft pulp mills operated by Boise-Cascade are separated by only a few hundred meters. Relying solely on ground-level meteorological data is somewhat precarious because of local turbulence especially close to the sources. It was therefore, advantageous to first scout the area for plumes of MeSH before choosing sampling sites for monitoring the Boise-Cascade Canadian mill.

Figure 6 shows the results of plume tracking data for MeSH taken September 28, 1983 between 10:09 and 11:27 hrs. During this period winds were out of the south at 5 to 20 km/hr. An examination of the instantaneous concentrations reveals two MeSH plumes, one originating from the U.S. mill and the other from the Canadian mill. Since only a limited amount of data was collected for the U.S. mill, the relative levels of DMS, DMDS and MeSH for the U.S plume were not established. Therefore, the MeSH levels shown in Figure 6 represent maximum instantaneous concentrations for the plume downwind of the U.S. mill. With a southerly wind, the plumes were distinguishable as far away as 8th Street. The MeSH plume boundaries from the Canadian mill were defined by Mowat Avenue east to Armit Avenue, and by Nelson Street north to 8th Street. Highest MeSH levels were recorded near Scott Street and Portage Avenue. The 1/2 hour averages acquired on September 28, 1983 (Table 5) reflect the concentration pattern evident in Figure 6, and show that the 1/2-hour standard for MeSH was exceeded in much of the area impacted by emissions from the Canadian mill.

4.3 **Monitoring Data Near the Boise-Cascade (U.S.) Insulite Plant**

On September 13 and 21, 1983 monitoring was conducted in the vicinity of the Boise-Cascade Insulite plant in International Falls, Minn. Both the GC (MAMU #2) and TAGA (MAMU #3) units were involved. Sampling (and analyses) were performed at locations directly downwind of the Insulite plant on Second Street in International Falls. Data was taken during periods of a visible emission episode; that is, when a white aerosol fog engulfed the MAMU.

The GC results were uneventful. Contaminants routinely monitored by the GC were not detected above their background levels. In contrast, the TAGA results showed more than 50 organic compounds which were tentatively identified from the real-time mass scans (see Tables 8a and 8b). The analyses of the TAGA mass spectra are interpretative, based on our knowledge of ion-molecule chemistry for a variety of chemical ionization reagents. Therefore, the compounds listed in Tables 8a and 8b are, at this stage, only suspected pollutants. Concentrations were again estimated from an instantaneous signal; they are provided to indicate the order-of-magnitude at which the substances occur. Clearly, additional monitoring of the Insulite emissions will be necessary to accurately identify and quantitate the major contaminants. For this particular application, more advanced monitoring equipment such as the TAGA 6000 system should be used.

4.4 Boise-Cascade Kraft Mill (U.S.)

The small amount of data for the Boise-Cascade (U.S.) kraft mill indicated that DMDS was a significant portion of the TRS compounds. Table 9 contains the results; since a lack of time prevented a MeSH measurement at site 21, the H_2S and adjusted TRS levels could not be determined. Site 47 did show significant levels of MeSH but MAMU #2 was not present on that occasion to measure TRS so, again, the H_2S level could not be determined.

4.5 Chlorine/Chlorine Dioxide Measurements

The emissions of Cl_2/ClO_2 from the Boise-Cascade (Can.) mill are believed to be highly variable and under normal operation the ambient air concentrations are expected to be low; that is, less than the Ministry standards of 300 ug/m^3 for Cl_2 and 85 ug/m^3 for ClO_2. In the operation of TAGA it was not possible to monitor simultaneously sulfur species and chlorine, and since the former was of higher priority, there was insufficient monitoring time to obtain representative levels of chlorine. Nevertheless, October 1, 1983 was devoted to Cl_2/ClO_2 monitoring, when 1/2-hour averages were acquired at four sites downwind of Boise-Cascade. Table 10 is a summary of our findings. The maximum 1/2-hour averages were 5.5 and 0.38 ug/m^3 for Cl_2 and ClO_2, respectively; these levels are well below the Ministry standards.

5.0 Tables and Figures

Table 1. Reduced Sulfur Compounds at Lagoon - 1/2-hour averages
Table 2. GC Results at Lagoon - 1/2-hour averages
Tables 3a, 3b. TAGA mass scans at Lagoon, + and - modes
Table 4. Hi-Volume Results at Lagoon
Table 5. Reduced Sulfur Compounds at Kraft mill (Can.) - 1/2-hour averages
Table 6. GC Results at Kraft mill (Can.) - 1/2-hour average
Tables 7a, 7b. TAGA mass scans at Kraft mill (Can.), + and - modes
Tables 8a, 8b. TAGA mass scans at Insulite (U.S.), + and - modes
Table 9. Reduced Sulfur Compounds at Kraft mill (U.S.) - 1/2-hour averages
Table 10. Chlorine/Chlorine Dioxide Results at Kraft mill (Can.) - 1/2-hour averages.

Figure 1. TAGA 3000 system schematic
Figure 2. Monitoring sites for 1/2-hour averages (on Map)
Figure 3. TAGA, plume tracking (DMDS) at lagoon; Sept. 29, 1983
Figure 4. TRS 1/2-hour averages, Kraft pulp mill (Can.)
Figure 5. MeSH 1/2-hour averages, Kraft pulp mill (Can.)
Figure 6. TAGA, plume separation (MeSH), Can. and U.S. Kraft mills, Sept. 28, 1983.

Table 1: Fort Frances Survey September 1983
Half-hour Averages - Reduced Sulfur Compounds
Source: Boise Cascade-Lagoon

Site*	Location	Time Period	Comments	Measured TRS	Concentration (ppb)				Adjusted TRS
					TAGA Measurements			Est.	
					MeSH	DMS	DMDS	H_2S	
			TRS Converter efficiency →		45%	12%	20%	70%	
1	1244 Cornwall	10 - Sep - 83 13:43 - 14:03	strong winds foam airbourne	8	-	5	14	5	24
2	Lagoon north end	10 - Sep - 83 15:39 - 16:09	strong winds foam airbourne	16	-	13	37	9	59
4	1248 Cornwall	11 - Sep - 83 10:41 - 11:11	odours noticable	2	-	3	6	1	10
7	Lagoon north end	11 - Sep - 83 13:36 - 14:06	strong odours	11	-	14	40	3	57
12	Lagoon south end near inlet	12 - Sep - 83 11:12 - 11:42	variable light winds strong odours	27	-	-	-		
		12:22 - 13:52		15	-	15	44	5	64
13	1048 Cornwall	12 - Sep - 83 14:39 - 15:09		-	-	4	19	-	23

* see Figure 2.

Table 1: Con'td

Site	Location	Time Period	Comments	Concentration (ppb)					Adjusted
				Measured	TAGA Measurements			Est.	
				TRS	MeSH	DMS	DMDS	H_2S	TRS
15	Lagoon South end near inlet	13 - Sep - 83 10:26 - 10:56		15	-	10	68	1	79
16	Lagoon South end near inlet	13 - Sep - 83 12:35 - 13:05	Sampling hose near lagoon surface	50	-	7	160	24	191
22	Lagoon opp. west aerators	22 - Sep - 83 12:10 - 12:40	opp. aerators	31	-	-	-	-	-
		13:23 - 13:53		17	-	15	62	4	81
23	Cornwall/8th	22 - Sep - 83 15:11 - 15:41		8	-	6	15	7	28
24	Walker/6th	22 - Sep - 83 15:59 - 16:29	wind shifting	4	-	2	3	4	9
48	York/8th	29 - Sep - 83 11:34 - 12:04	Lagoon foam airbourne	8	-	6	7	8	21
49	Lillie/6th	29 - Sep - 83 13:26 - 13:56	Winds light	-	-	2	2	0	4

TABLE 2

GC Results at Boise-Cascade Secondary Treatment Facility (Lagoon)

1/2 hour average (ug/m^3) Fort Frances - September 1983

Compound	Set #1-Sept.10 12:13-12:43	Set #2-Sept.13 10:59-11:29	Set #3-Sept.13 12:28-12:58	Set #4-Sept.22 11:55-12:25	Min Det. Lim
Pentane	10	6	6	22	6
3-Methylpentane	Not Detected	N.D.	N.D.	N.D.	7
Hexane	N.D.	N.D.	N.D.	N.D.	7
Benzene	8	17	13	21	7
Iso-octane	16	22	12	15	5
Heptane	N.D.	N.D.	N.D.	N.D.	8
Toluene	16	18	12	17	7
Octane	N.D.	N.D.	N.D.	N.D.	12
Ethylbenzene	N.D.	N.D.	N.D.	16	10
p + m - xylene	23	16	N.D.	23	9
O-xylene	14	N.D.	N.D.	16	12
Isopropylbenzene	N.D.	N.D.	19	19	14
Decane	N.D.	N.D.	N.D.	N.D.	32
Chloroform	N.D.	N.D.	616	N.D.	65
n-propylbenzene	N.D.	N.D.	63	N.D.	14
Location	Lagoon inlet	Lagoon inlet	Lagoon inlet with sampling hose	Beside aerators	

Note: see Appendix 3 for existing standards, guidelines, and threshold limit values.

Table 3a

Analyses of TAGA Mass Scans (Positive Mode)
Boise-Cascade Lagoon Sites
Fort Frances, September 1983

Mass	Ion Assignment	Tentative Identity	Estimated Conc. (ppb)			
			Set #1 Inlet	Set #2 Inlet	Set #3 Inlet	Set #4 Aerator
33	CH_50^+	methanol	20	4	40	2
47	$C_2H_7O^+$	ethanol	ND	ND	1	ND
62	$C_2H_6S^+$	dimethyl-sulfide	10	10	2	1
73	$C_4H_9O^+$	butanone/ butanal	ND	1	1	ND
94	$C_2H_6S_2^+$	dimethyl-disulfide	2	10	25	20
137	$C_{10}H_{17}^+$	pinenes	1	1	1	1
153	$C_{10}H_{17}O^+$	camphor/ isomers	1	2	2	5

Note: See Table 2 for monitoring times. These concentrations are instantaneous values within the monitoring period.

Table 3b

Analyses of TAGA Mass Scans (Negative Mode)
Boise-Cascade Lagoon Sites
Fort Frances, September 1983

Mass	Ion Assignment	Tentative Identity	Estimated Conc. (ppb) Set #1 Inlet	Set #2 Inlet	Set #3 Inlet	Set #4 Aerator
35	Cl^-	any chlorine species	ND	10	3	1
45	HCO_2^-	formic acid	10	20	20	5
59	$CH_3CO_2^-$	acetic acid/ acetaldehyde	ND	40	ND	ND
73	$C_2H_5CO_2^-$	propanoic acid/ propanal	1	3	6	ND
89	$C_3H_4O_3^-$	pyruvic acid	ND	1	ND	ND
95	$CH_3SO_3^-$	DMDS/DMS/MeSH	2	40	80	30

Note: See Table 2 for monitoring times. These concentrations are instantaneous values within the monitoring period.

TABLE 4. Hi-Volume Results; Fort Frances, 1983

Date (Start)	Time[2]	Location	Filter#	TSP(ug/m^3)
Sept. 11	10:50-10:50	1246 Cornwall Road	126	5
12th	11:00-11:00	1246 Cornwall Road	128	6
12th	11:15-11:15	30 York St. at 8th	129	41
13th	11:20-11:20	1246 Cornwall Road	131	9
26th	17:10-17:10	Lagoon	X-01	- (Sterile)[1]
"	17:10-17:10	Lagoon	X-08	419
"	17:40-17:40	Cemetery	X-03	- (Sterile)
"	17:40-17:40	Cemetery	X-09	112
27th	17:15-17:15	Lagoon	X-04	- (Sterile)
"	17:15-17:15	Lagoon	X-11	148
"	17:45-17:45	Cemetery	X-05	- (Sterile)
"	17:45-01:45	Cemetery	X-10	57
Oct. 2	10:15-10:15	Lagoon	X-14	- (Sterile)
"	10:15-10:15	Lagoon	X-17	5
"	09:45-09:45	Cemetery	X-16	- (Sterile)
"	09:45-09:45	Cemetery	X-18	5

Note: 1: Sterile filters were used for bacterial analyses only.

Note 2: All 24-hour periods except filter X-10 (8-hours).

TABLE 5: Fort Frances Survey September 1983
Half-hour Averages - Reduced Sulfur Compounds
Source: Boise-Cascade (Can.) Plant

Site*	Location	Time Period	Comments	Concentration (ppb)					Adjusted
				Measured TRS	TAGA measurements			Est.	
					MeSH	DMS	DMDS	H_2S	TRS
			TRS Converter efficiency	→	45%	12%	20%	70%	
26	Portage, South of Nelson	23-Sept-83							
		11:12 - 11:42	TRS odours	34	81	-	-	0	88
		11:47 - 12:17	GC samples	-	-	7	N.D.		
27	423 1st St.	23 - Sep - 83							
		12:50 - 13:20		8	14	-	-	2	19
		13:24 - 13:54		11	-	3	N.D.		
28	Church/Victoria	23 - Sep - 83							
		14:11 - 14:41		12	37	-	-	0	41
		14:47 - 15:17		-	-	4	N.D.		
29	317 Nelson	23 - Sep - 83							
		15:54 - 16:24		-	44	-	-	0	46
		16:27 - 16:57		12	-	2	N.D.		
30	Church/Portage	24 - Sep - 83	TRS odour						
		11:03 - 11:33	MAMU # 2 only	44	-	-	-	-	110[1]
		11:33 - 12:03	GC sample	43	-	-	-	-	110[1]
		12:03 - 12:33	" "	28	-	-	-	-	63[1]
	328 1st St.	14:15 - 14:45	MAMU 2 only	28	-	-	-	-	-

* see Figure 2.

Note 1: Since MAMU #3 (TAGA) was not present at sites 30 and 39, a multiplication factor of 2.5 has been applied to the "Measured TRS" numbers merely to indicate the probable "Adjusted TRS" levels. The factor 2.5 is an approximation extracted from data elsewhere in Table 5.

TABLE 5: Cont'd

Site	Location	Time Period	Comments	Concentration (ppb)					Adjusted
				Measured TRS	MeSH	DMS	DMDS	H_2S	TRS
31	Church/Portage	24-Sep-83							
		14:24 - 14:54		-	27	-	-		
		14:56 - 15:26		37	-	5	-	36	63
32	Christie/3rd	24 - Sep - 83							
		16:14 - 16:44		7	16	-	-	0	16
		16:53 - 17:23		N.D.	-	1	N.D.		
33a	Church/Victoria	24 - Sep - 83							
		17:54 - 18:24	MAMU #2 only	11	-	-	-	3	23
33b	Victoria, North of Church	17:40 - 18:10		-	20	-	-		
		18:13 - 18:43		6	-	1	-		
37	Nelson	25 - Sep - 83							
		23:06 - 23:36	Directly opposite	35	68	-	-	6	74
		23:38 - 00:08	Kraft Mill	3	-	N.D.	N.D.		
39	Nelson/Mowat	27- Sep - 83							
		09:37 - 10:07	MAMU #2 only	28	-	-	-		70*
		10:07 - 10:37	" "	29	-	-	-		72*
		10:37 - 11:07	" "	17	-	-	-		42*

* see note 1 on previous page.

TABLE 5: Cont'd

Site	Location	Time Period	Comments	Measured TRS	Concentration (ppb)				Adjusted TRS
					MeSH	DMS	DMDS	H_2S	
40	Church/Central	27-Sep-83							
		12:11 - 12:41		24	60	-	-	0	60
		12:53 - 13:23		-	-	2	N.D.		
41	Cornwall/5th	27 - Sep - 83							
		13:51 - 14:21	recovery boiler	15	7	-	-	16	23
		14:24 - 14:54	plume impinging	25	-	N.D.	N.D.	29	36
42	801 Central	27 - Sep - 83							
		15:14 - 15:44		17	29	-	-	5	34
		15:46 - 16:16		15	-	1	N.D.		
44	Church/Portage	28 - Sep - 83							
		10:34 - 11:04	MAMU #2 only	19	-	-	-		
		11:04 - 11:34	" "	13	-	-	-		
		12:04 - 12:34		17	25	-	-	8	33
		12:39 - 13:09		8	-	N.D.	5		
45	1st/Victoria	28 - Sep - 83							
		13:31 - 14:01	intermittent rain	11	24	-	-	0	24
		14:04 - 14:34		21	-	2	3	14	40
46	Nelson/Portage	28 - Sep -83							
		14:52 - 15:22		39	77	-	-	5	82
		15:24 -15:54		20	-	N.D.	4		

TABLE 6

GC Results at Boise-Cascade Kraft Mill (Can)
1/2 hour average (ug/m^3) Fort Frances, - September 1983

Compound	Set 5-Sept.23 10:56-11:26	September 23 11:26-11:56	September 24 11:47-12:17
Pentane	8	15	27
3-Methylpentane	N.D.	N.D.	9
Hexane	N.D.	N.D.	16
Benzene	15	13	32
Iso-octane	8	10	44
Heptane	N.D.	N.D.	24
Toluene	14	11	57
Octane	N.D.	N.D.	27
Ethylbenzene	17	11	58
p + m - xylene	29	23	151
o-xylene	22	14	94
Isopropylbenzene	N.D.	N.D.	40
Decane	N.D.	N.D.	N.D.
Chloroform	N.D.	N.D.	N.D.
n-propylbenzene	N.D.	N.D.	N.D.
Location:	Portage Ave. & Nelson St.	Portage Ave. & Nelson St.	Portage Avenue & Church Street
Wind: km/hr/Dir	7/210°	7/200°	9/180°

Note: see Appendix 3 for existing standards, Guidelines, and threshold limit values.

Table 7a

Analyses of TAGA Mass Scans (Positive Mode)
Boise-Cascade (Can.) Kraft Mill
Fort Frances, September 1983[1]

Mass Peak	Ions Assignment	Tentative Identity	Estimated Conc. (ppb) Set #5
33	CH_4O^+	methanol	30
62	$C_2H_6S^+$	dimethyl sulfide	10
79	$C_2H_7SO^+$	dimethyl sulfoxide	1
92	$C_7H_8^+$	toluene	10
94	$C_2H_6S_2^+$	dimethyl disulfide	4

Note 1: See Table 6 Set #5 for monitoring times and location. These concentrations are instantaneous values during the monitoring period.

Table 7b

Analyses of TAGA Mass Scans (Negative Mode)
Boise-Cascade (Can.) Kraft Mill
Fort Frances, September 1983[1]

Mass Peak	Ions Assigment	Tentative Identity	Estimated Conc. (ppb) Set #5
67	ClO_2^-	chlorine dioxide	5
70	Cl_2^-	chlorine	5
95	$CH_3SO_3^-$	MeSH	20

Note 1: See Table 6 Set #5 for monitoring times and location. These concentrations are instantaneous values during the monitoring period.

Table 8a

Analysis of TAGA Mass Scans (positive mode)
Boise Cascade - Insulite Plant
International Falls, Minn. U.S.A.
September 1983

Mass Peak	Ion Assignment	Tentative Identity	Estimated Conc. (ppb) Set #1	Set #2
33	CH_4O^+	methanol	40	10
59	$C_3H_7O^+$	acetone/ propanal	10	10
60	$C_3H_{10}N^+$	C3 alkyl amine	2	1
61	$C_2H_5O_2^+$ $C_3H_9O^+$	acetic acid propanol	2	3
71	$C_4H_7O^+$	methyl vinyl ketone/ butenal/vinyl ether	1	2
73	$C_4H_9O^+$	methyl ethyl ketone/ . butanol/tetra hydro furan	ND	1
74	$C_4H_{12}N^+$	C_4 alkyl amine	1	1
75	$C_4H_{11}O^+$	butanol/ diethyl ether	1	2
	$C_3H_7O_2^+$	propionic acid/ methyl formate		
85	$C_5H_9O^+$	cyclopentanone	3	3

Table 8a (Cont'd)

Mass Peak	Ion Assignment	Tentative Identity	Estimated Conc. (ppb) Set #1	Set #2
87	$C_4H_7O_2^+$ $C_5H_{11}O^+$	methylacrylate cyclopentanol C5 ketones C5 aldehydes	1	1
94	$C_2H_6S_2^+$	dimethyl sulfide	ND	20
	$C_6H_6O^+$	phenol		
97	$C_5H_5O_2^+$ $C_6H_9O^+$	furfural dimethyl furan	10	10
99	$C_4H_3O_3^+$	maleic anhydride/ furfuryl alcohol	3	2
101	$C_5H_9O_2^+$ $C_6H_{13}O^+$	ethyl acrylate MBK/MIBK hexanone/ cyclohexanol	1	1
111	$C_6H_7O_2^+$	resorcinol	10	10
113	$C_6H_9O_2^+$	dihydro resorcinol	3	1
	$C_7H_{13}O^+$	cycloheptanone		
115	$C_7H_{15}O^+$	heptanone/ heptanal	1	1
117	$C_6H_{13}O_2^+$	butyl acetate	1	1

Table 8a (cont'd)

Mass Peak	Ion Assignment	Tentative Identity	Estimated Conc. (ppb) Set #1	Set #2
127	$C_6H_7O_3^+$	trihydroxyl benzene/ hydroxyl methyl-furaldehyde	4	1
128	$C_{10}H_8^+$	napthalene	1	1
153	$C_{10}H_{17}O^+$	camphor/ decadienone	2	1

Note: Set #1 13-Sept-83; 17:00-17:20 hrs.
Set #2 21-Sept-83; 14:40-15:00 hrs.
These concentrations are instantaneous values during the monitoring period.

Table 8b

Analysis of TAGA Mass Scans (Negative Mode)
Boise-Cascade - Insulite Plant
International Falls, Minn. USA
September 1983

Mass Peak	Ion Assignment	Tentative Identity	Estimated Conc. (ppb) Set #1	Set #2
26	CN^-	any cyano species	?	ND
35	Cl^-	any chlorine species	?	ND
45	HCO_2^-	formic acid	10	100
59	$CH_3CO_2^-$	acetic acid/ acetaldehyde	40	1,000
73	$C_2H_5CO_2^-$	propanoic acid/ propanal	1	10
87	$C_3H_7CO_2^-$	butanoic acid/ butanal	ND	2
89	$C_3H_50_3^-$	lactic acid	1	4
93	$C_6H_50^-$	phenol	1	ND
99	$C_5H_70_2^-$	pentenoic acid/ pentenal	ND	2
109	$C_6H_50_2^-$	resorcinol	ND	1
121	$C_7H_50_2^-$	benzoic acid/ benzaldehyde	ND	5

Note: These concentrations are instantaneous values during the monitoring period.

TABLE 9: Fort Frances Survey September 1983
Half-hour Averages - Reduced Sulfur Compounds
Source: Boise-Cascade (U.S.) Plant

Site	Location	Time Period	Comments		Concentration (ppb)				Adjusted
				TRS	MeSH	DMS	DMDS	H_2S	TRS
21	2nd St./2nd Ave.	21 - Sep - 83							
		17:28 - 17:58	rain intermittent	27	-	8	10		
47	U.S. Customs	28 - Sep - 83							
		16:40 - 17:10	MAMU #3 only	-	-	4	12		
		17:14 - 17-44	Insulite odours also present	-	26	-	-		

Table 10

Chlorine/Chlorine Dioxide Monitoring (MAMU No. 3)
Boise-Cascade (Can.) Kraft Pulp Mill
Fort Frances, October 1, 1983

			Met. Data[1]			Concentration in ug/m^3	
Site	Time	Location	WD	WS	AT	Cl_2	ClO_2[2]
51	11:10-11:40	426 Front St.	WNW	1.5	11	2.8	0.22
52	11:48-12:18	Front/Victoria	WNW	14	11	5.5	0.38
53	13:31-14:01	Front/Armit	WNW	4	12	1.6	0.14
54	14:15-14:45	410 Nelson[3]	WNW	8	12	0.08	0.04

Note 1: 30 minute average; WS in km/hr, AT in °C.
2: calibration based on Cl_2 - estimate only
3: outside plume boundary

TAGA 3000 SYSTEM

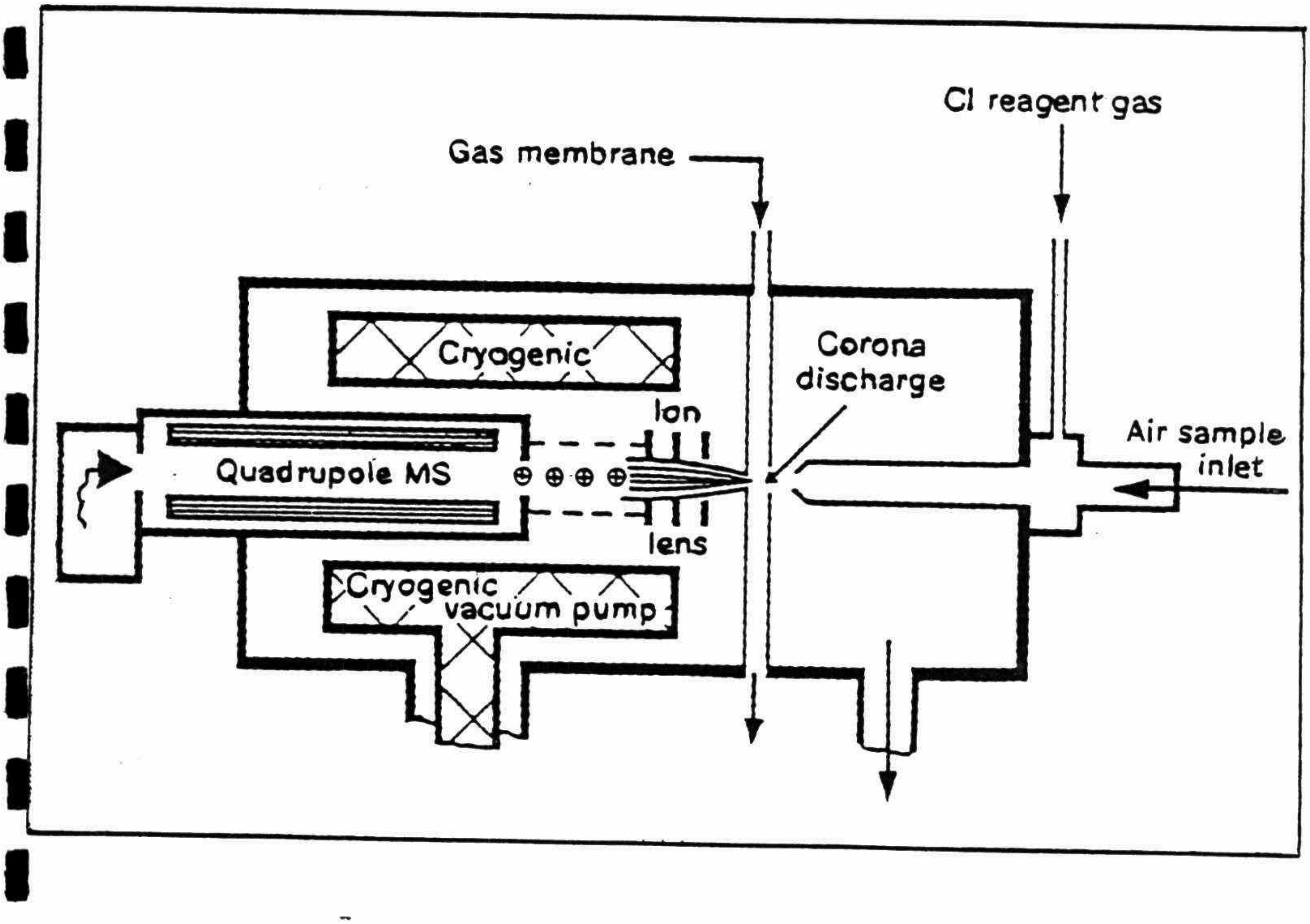

FIGURE 1: SCHEMATIC OF THE TAGA 3000 SYSTEM USED IN MAMU #3.
DIRECT AIR SAMPLING (APCI) CONFIGURATION.

FORT FRANCES SURVEY 1983

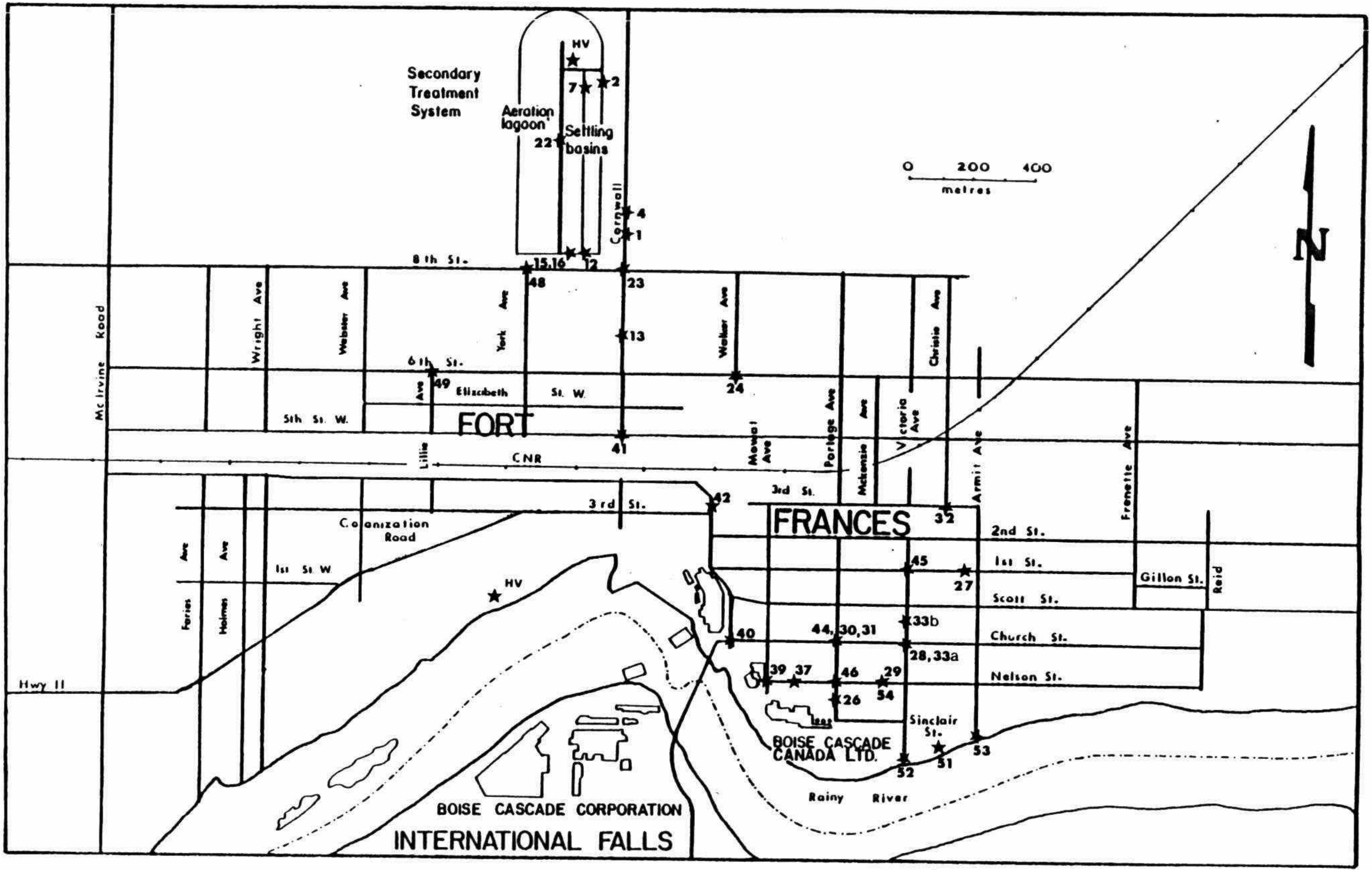

FIGURE 2: MONITORING SITE LOCATIONS
1/2 HOUR AVERAGES
MAMU #2 AND MAMU #3

FORT FRANCES SURVEY 1983

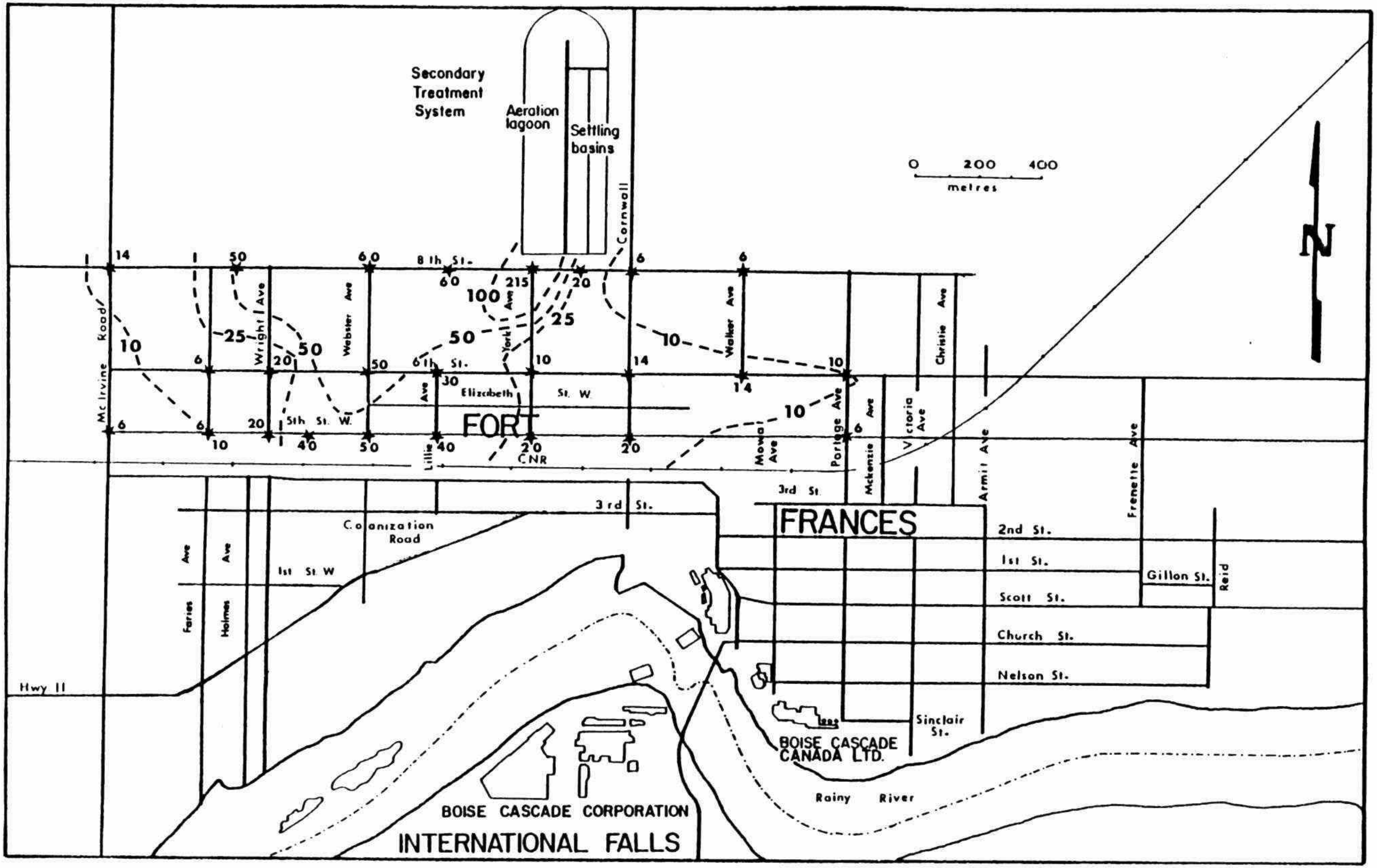

FIGURE 3: MAMU #3 (TAGA) PLUME TRACKING DATA - DMDS
INSTANTANEOUS READINGS (ug/M3)
SOURCE: BOISE CASCADE - LAGOON
29-SEP-83, 10:55 - 11:30 HRS. NE WINDS 5-20 KM/HR.
(10 ug/M3 = 2.6 ppb)

FORT FRANCES SURVEY 1983

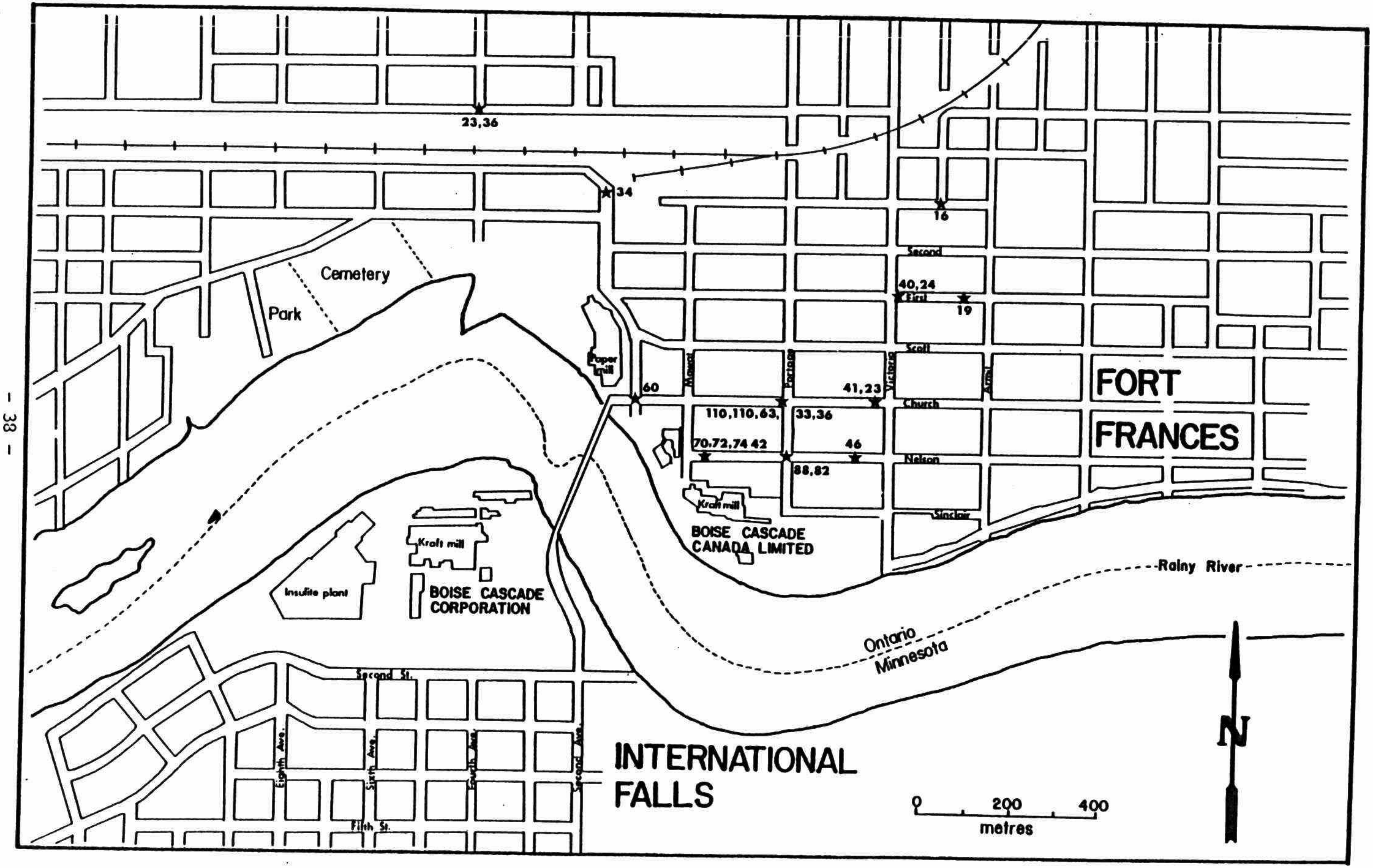

FIGURE 4: TOTAL REDUCED SULFUR (TRS, ADJUSTED)
1/2 HOUR AVERAGES (ppb)

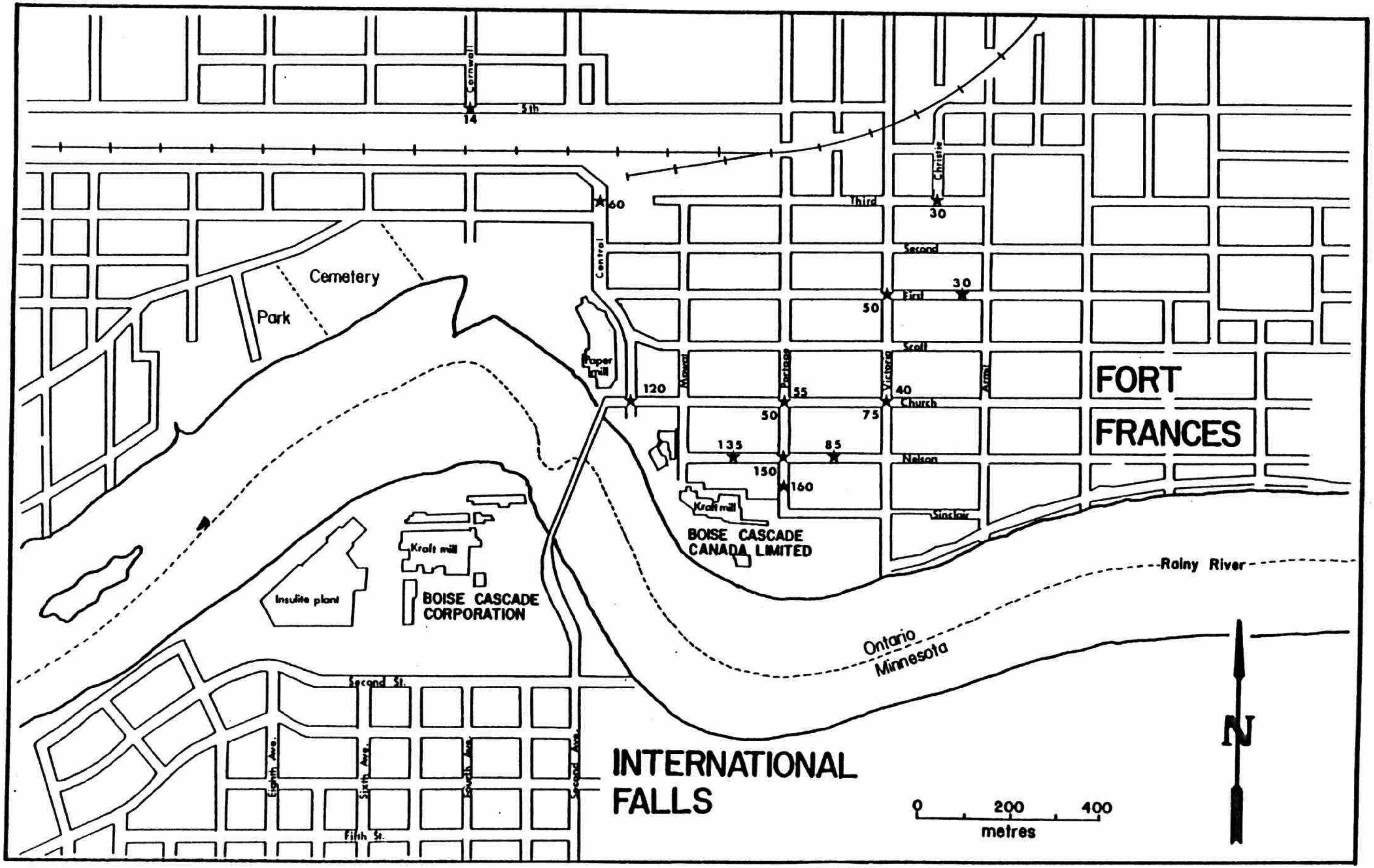

FIGURE 5: METHYL MERCAPTAN CONCENTRATIONS
1/2 HOUR AVERAGES (ug/M3)
MAMU #3 (TAGA)

FORT FRANCES SURVEY 1983

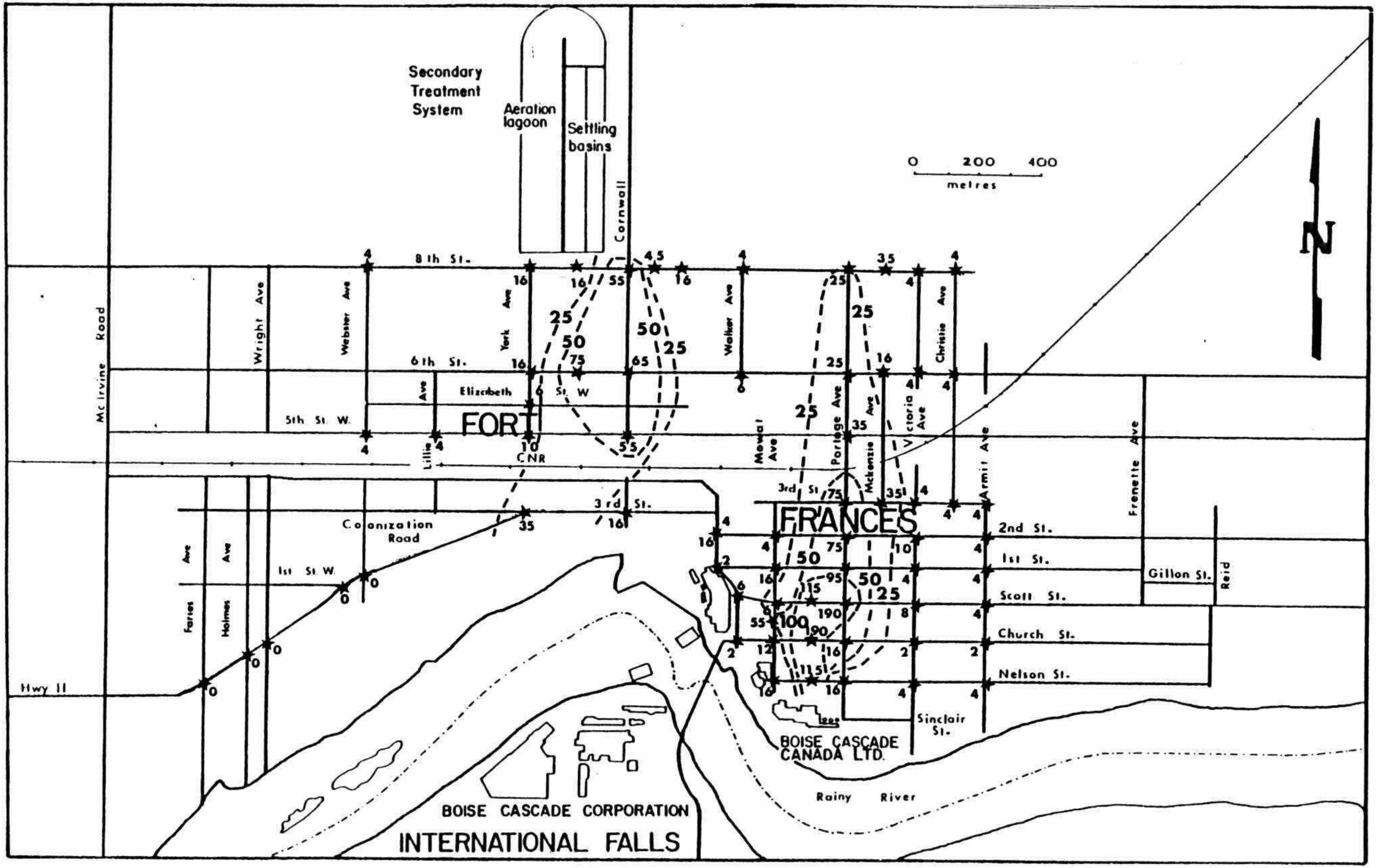

FIGURE 6: MAMU #3 (TAGA) PLUME TRACKING DATA - MeSH
INSTANTANEOUS READINGS (ug/M3)
SOURCES: BOISE CASCADE U.S. AND CAN. PLANTS
28-SEP-83, 10:09 - 11:27 HRS, SOUTH WINDS 5-20 KM/HR.
[illegible] ug[illegible]= 5[illegible]pb)

APPENDIX 1

Microbiologist's Report on Bacterial Levels in Dried Foam

BACTERIAL LEVELS IN DRIED FOAM
BOISE CASCADE CANADA LTD., FORT FRANCES
SEPTEMBER, 1983

The collection of a single grab sample of dried foam which had blown from the aeration lagoon, Boise Cascade Canada Ltd., initiated a further study into the bacterial densities in this material.

GRAB SAMPLE

1. Sample Collection

On September 14, 1983, a grab sample of dried foam (approximate total weight: 15-20 g) was collected in a wide-mouth jar. This sample of dried foam was brown in colour and occupied a volume of approximately 150-220 cc. It was composed of individual fine particles which flew easily into the air. This sample was received at the laboratory late in the afternoon on September 16, 1983. Bacteriological analysis was started on Monday, September 19, 1983.

2. Materials and Methods

One gram of dried foam was transferred in 99 ml of sterile phosphate buffered dilution water and shaken for 30 minutes on a wrist shaker to rehydrate the foam. It was noted that the dried foam could be rehydrated only with some difficulty. Appropriate dilutions of the rehydrated foam were prepared and analyzed by membrane filter (MF) analysis and most probable number (MPN) analysis. Standard techniques were used in all cases. The following bacterial parameters were tested.

MEMBRANE FILTER ANALYSIS

Parameter	Media	Incubation
Total coliform (TC)	m-endo agar LES	22 hr. @ 35°C
Fecal coliform (FC)	m-TEC agar	23 hr. @ 44.5°C
Escherichia coli (EC)	m-TEC-IG agar	23 hr. @ 44.5°C
Fecal streptococcus (FS)	m-enterococcus agar	48 hr. @ 35°C
Pseudomonas aeruginosa (PsA)	m-PA-E agar	48 hr. @ 41.5°C
Heterotrophic bacteria 35 (HB35)	m-SPC agar	48 hr. @ 35°C

MOST PROBABLE NUMBER ANALYSIS

Parameter	Media	Incubation
Total coliform	LTB/BGB	24-48 hr. @ 35°C
Fecal coliform	LTB/EC	24-48 hr. @ 35°C/44.5°C
Pseudomonas aeruginosa	Drakes/SMA	96 hr. @ 35°C

3. Results

The bacteriological results are listed in Table 1.

TABLE 1. Bacterial concentrations in grab sample of dried foam.

Parameter	Method	Density per gram (dry/wt.)
TC	MF	L1000
	MPN	92,000
FC	MF	L1000
	MPN	L100
EC	MF	L1000
	-	-
FS	MF	L1000
	-	-
PSA	MF	L1000
	MPN	490
HB35	MF	150,000
	-	-
Growth in LTB	MPN	9,200,000

With the exception of the HB35 count, no target bacterial groups were recovered using the MF method. Target bacterial groups were recovered only with the MPN method. No fecal coliform bacteria were recovered by either method. Several of the LTB tubes were streaked to isolate and identify the bacterial species. All identifications employed the API-20E system.

The predominant coliforms in the dried foam sample were Enterobacter sakazaki and Enterobacter agglomerans, both occurring at the 1 x 10^5 dilution level. Several other organisms were isolated but could not be identified by the identification system used. Organisms occurring at higher concentrations were quite inert biochemically.

HI-VOL FILTER SAMPLES

In an attempt to quantify the amount of dried foam that was being blown from the aeration site onto surrounding property, two Hi-Vol filter stations were established. One station was set up near the lagoon and a second station was set up at the cemetery and acted as a control station.

1. Sample Collection

Sterile Hi-Vol filter cartridges were prepared in the laboratory by autoclaving. These filters cartridges were taken into the field and attached aseptically to Hi-Vol filter motor units. Matched pairs of filters (i.e.: one from the lagoon and one from the cemetery) were collected over three 24-hour periods on September 26, September 27 and October 2, 1983. All Hi-Vol units were operated at 40 CFM.

2. Materials and Methods

Following receipt at the laboratory, the particulates on the filter surface were aseptically scraped off, weighed and dilutions prepared. An MPN analysis was set up for TC and FC. Only the filters collected September 26, 1983 were analyzed for bacterial levels.

3. Results

The appearance of the Hi-Vol filters upon receipt at the laboratory is listed in Table 2.

TABLE 2. Physical appearance of the Hi-Vol filters after exposure.

Sampling Day	Lagoon	Cemetery
September 26	Foam particles 2-3 mm deep on surface of filter. Particulates are brown and identical in appearance to the grab sample of dried foam.	Particulates are grey in colour and mostly embedded in the filter.
September 27	Filter is incompletely covered with foam particles. Amount of material on the filter is only 1/100 to 1/1000 of that for September 26.	As above.
October 2	Foam particles are less than on September 27.	Particulates are very light grey. Filter is mainly white.

Only the filter collected September 26 at the lagoon showed a marked accumulation of dried foam. The bacteriological results are listed in Table 3.

TABLE 3. Bacterial levels in Hi-Vol filter samples, September 26, 1983.

Parameter	Density per gram (dry wt.)	
	Lagoon	Cemetery
TC	L200	L200
FC	L200	L200
Growth in LTB	$\hat{=}$200	L200

No indicator organisms were recovered from the material collected by the Hi-Vol filters. In fact, the level of viable bacteria capable of growing in the total coliform MPN medium was so low that only one tube showed growth of any kind.

DISCUSSION OF RESULTS

Significant levels of bacteria were able to survive in the grab sample of dried foam collected near the lagoon. This was the state that the dried foam would most likely be observed in as it was blown to nearby locations. Extremely low levels of bacteria were recovered from the material on the Hi-Vol filters. This may represent an anomally as a result of extreme drying of the foam by the Hi-Vol filter fan and might not be representative of the true situation.

It is almost impossible to compare bacterial levels in the dried foam sample of September 14 with those samples collected in 1980 because a different unit of measure had to be used. In the current study, the levels were based on a dry weight. In the earlier study, a wet basis was used because the foam was received wet and artificially dried in the laboratory. A one gram sample of dried foam occupies an unexpectedly large volume (approximately 50 cu. cm.).

Curiously, *Klebsiella pneumoniae* was not recovered from the dried foam. It was the predominant organism in the previous study. It is probable that larger populations of bacteria could have been recovered from the grab sample had it been analyzed shortly after collection instead of one week later.

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APPENDIX 2

Complete Gas Chromatograph Results

TABLE 11: GC RESULTS (ug/m^3) FORT FRANCES 1983

Compound	September 11					September 12		September 13			
	1035- 1105	1105- 1135	1213- 1243	1257- 1327	1330- 1400	1041- 1111	1551- 1621	1029- 1059	1059- 1129	1143- 1213	1228- 1258
Pentane	16	10	10	8	6	25	22	10	6	6	6
3-Methylpentane						13	9	7			
Hexane	12					19	13	12			
Benzene	20	19	8	15		35	26	20	17	7	13
Iso-octane	25	29	16	22	8	41	28	28	22	7	12
Heptane	12	8				21	11	15			
Toluene	28	20	16	15	8	49	32	29	18	10	12
Octane						14					
Ethylbenzene	18					32	17	27			
p + m -xylene	33	19	23	14	11	62	37	43	16	12	
o -xylene	22		14			41	22	31			
Isopropylbenzene						20		21		18	19
Decane						36		35			
Chloroform										696	616
n-propylbenzene										62	63
Comment/Location	Cornwall Rd at Lagoon		Lagoon Inlet	Inside-east Road at Lagoon		Lagoon Inlet W-side	York St. at 6th	Lagoon Inlet		Lagoon Inlet with sampling hose. One unknown between Heptane-Toluene.	

TABLE 12: GC RESULTS (ug/m^3) FORT FRANCES 1983

Compound	Sept. 13 1704- 1734	September 14 1715- 1745	 1745- 1815	September 21 1440- 1510	 1125- 1155	September 22 1155- 1225	 1234- 1304	September 23 1056- 1126	 1126- 1156	Sept.24 1147- 1217	Stand. (S) Guidel.(G)	Min. Det.
Pentane	27	41	60	14	13	22	8	8	15	27		6
3-Methylpentane	12	18	24							9		7
Hexane	16	25	26		9					16	35,000 G	7
Benzene	47	58	81	10	20	21	8	15	13	32	10,000 S	7
Iso-octane	25	52	48	6	14	15		8	10	44		5
Heptane	12	23	17		11					24		8
Toluene	39	62	63	9	23	17	13	14	11	57	2,000 S	7
Octane		15			13					27		12
Ethylbenzene	17	34	22		22	16		17	11	58	4,000 S	10
p + m - xylene	44	80	51	21	45	23	22	29	23	151	2,300 S	9
o - xylene	26	48	23		35	16	16	22	14	94		12
Isopropylbenzene		16			28	19	31			40	100 Prov. G	14
Decane	36											32
Chloroform											1,500 G	65
n-propylbenzene												14
Comment/Location	30 min. sample at 30 ml/min Insulite				Lagoon at Aerators			Kraft Mill, Large TRS				

APPENDIX 3

Ontario standards, guidelines, and occupational health threshold limit values for compounds monitored in the Fort Frances International Falls survey

TABLE 13

Standards and Guidelines for Contaminants Detected in Fort Frances, 1983

Compound	Standard (S) / Guideline (G) (ug/m^3)
Acetic Acid	2,500 S
Acetone	48,000 S
Benzene	10,000 S
Butanone	31,000 S
Chlorine	300 S
Chlorine Dioxide	85 S
Chloroform	1,500 G
Dimethyl Disulfide	40 S (= 10.4 ppb)
Dimethyl sulfide	30 S (= 11.8 ppb)
Ethanol	19,000 G
Ethyl Acrylate	4.5 S
Ethylbenzene	4,000 S
Formaldehyde	65 S
Formic Acid	1,500 S
Furfural	1,000 S
Furfuryl Alcohol	3,000 S
Hexane	35,000 G
Hydrogen Sulfide	30 S (= 21.5 ppb)
Isopropylbenzene	100 G
Maleic Anhydride	100 G
Methanol	84,000 S
Methylacrylate	4.0 S
Methyl Isobutyl Ketone	1,200 G
Methyl Mercaptan	20 S (= 10.2 ppb)
Phenol	100 S
Propanol	48,000 G
Propionic Acid	100 G
Tetra Hydro Furan	93,000 S
Toluene	2,000 S
Xylene	2,300 S

TABLE 14

Threshold Limit Values for Contaminants Detected in Fort Frances 1983

Compound	Threshold Limit Value (mg/m^3) - Note 1
Acetaldehyde	180
Butanol	C 150 - Note 2
Butyl Acetate	710
Cyclohexanol	200
Diethyl Ether	1,200
Heptane	1,600
Heptanone	235
Hexanone	20
Methyl Formate	250
Napthalene	50
Octane	1,450
Pentane	1,800
Resorcinol	45

Note 1: Threshold Limit Value (TLV) - the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

Note 2: Threshold Limit Value C - The concentration that should not be exceeded even instantaneously.

Note 3: These TLV's are listed in Booklets published by:
(a) The American Conference of Governmental Industrial Hygienists (ACGIH), and
(b) The Ontario Ministry of Labour, Occupational Health and Safety Division.

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